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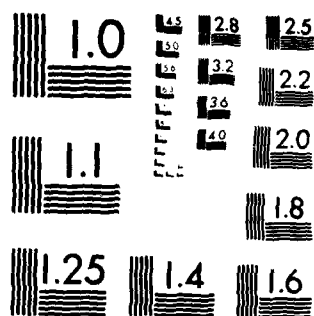
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TECHNICAL REPORT NO. 28Comparison of Equilibrium Internuclear Distances for
Diatomic Molecules and Their Ions

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Comparison of Equilibrium Internuclear Distances for
Diatomic Molecules and their Ions **

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Abstract

The equilibrium internuclear distances (EIDs) of several diatomic molecules (Ca, CN, Na, NO, O₂, F₂, F₂) and their ions are investigated. The EID dependence on electronic structure and on nuclear charges are examined separately and are shown to have systematic behaviors. The atomic radius overlap, which is defined as a sum of the two atomic radii minus the EID, plays an important role in understanding the systematic behaviors of the EIDs. The systematic behaviors found in this work can be used to predict unknown EIDs for diatomic molecules and their ions with equal or nearly equal nuclear charges. Based on these systematic behaviors, we predict the EID of the CN⁻ ground state to be 1.171 Å, the EID of the Ca⁺ ground state to be 1.24 Å, and the *6s* shape resonance peak of NO⁻ to be 15.2 eV.

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In this work, we restrict ourselves to diatomic

molecules and their ions with equal or nearly equal nuclear charges, that is, to the $|Z_1 - Z_2| \leq 1$ cases. Systematic behaviors discovered here may not be applicable to the $|Z_1 - Z_2| > 1$ cases.

2. Averaged EID for an electronic configuration

Tables 1 and 2 list term energies (T_n), EIDs, and state symmetries observed for Ca, CN, N₂, NO, O₂, F₂, and their ions. Data on the doubly-ionized ions are calculated by Hurley [1] with a semiempirical method. The EID of the $DF(2s^2, \pi)$ state in table 2 is also calculated theoretically by O'Hare and Wahl [2] with an ab initio CI method. These theoretical data in tables 1 and 2 are in parentheses. The remaining data are determined experimentally and are obtained from the tables compiled by Huber and Herzberg [3].

To assign electronic configurations (ECs) to the observed states, we have used, besides the number of electrons and the state symmetry, the following two facts.

- (1) Electronic states arising from an EC tend to have similar EIDs. (2) The energy splittings of these electronic states are nearly independent of the nuclear charges, Z , and Z_2 , if the difference, $|Z_1 - Z_2|$, is zero or one, such as the cases studied in this work. Furthermore, the weighted average energy of these electronic states are known approximately from the measured orbital binding energies.

1. Introduction

The equilibrium internuclear distances (EIDs) of several diatomic molecules (Ca, CN, N₂, NO, O₂, F₂) and their ions are investigated. When diatomic molecules are excited or ionized, their EIDs change in general. These changes (Δ EIDs) are understood qualitatively in terms of the bonding characters of the associated orbitals. To evaluate these changes quantitatively, however, one resorts to a theoretical calculation. In this work, we propose empirical methods to predict the Δ EIDs semi-quantitatively.

The Δ EIDs mentioned above are caused by the changes in the electronic structure while keeping the nuclear charges constant. In this work, we also investigate the Δ EIDs that are caused by changes in the nuclear charges while keeping the electronic structure constant. For both cases, we find new systematic behaviors. Based on these systematic behaviors, we predict the EID of the CN⁻ ground state.

We introduce a quantity called "atomic radius overlap (ARO)", which is defined as a sum of the two atomic radii minus the EID. We show that this ARO is a useful indicator of an averaged atomic orbital overlap in a molecule. We also show that molecules or ions that have the same electronic structure have the same ARO, regardless of their nuclear charges.

The ECs listed in tables 1 and 2 satisfy the above requirements and also agree with previous assignments (4).

In tables 1 and 2, the inner shells $1s$, $2s$, and $3s$ are assumed to be closed. For homonuclear molecules and their ions, the orbitals, $1s$, $2s$, $3s$, $4s$, $1s$, $5s$, and $2s$, should be interpreted as $1s$, $2s$, $3s$, $4s$, $1s$, $5s$, and $2s$, respectively. We adopt this convention throughout the paper.

The EIDs that belong to the same EC are averaged by weighting with the state degeneracies, and the results are listed in table 3. Averages calculated with theoretical EIDs are in parentheses. Some of the multiplet states arising from an EC are missing in table 2, for example, the $4p^2$, $4p$, and $4s$ states from the $4p^2$ configuration. Averaging with these incomplete multiplet data could introduce a significant error. Table 3 expresses the EIDs as a function of 6 variables, namely two nuclear charges and four orbital occupation numbers. In the following sections, we analyze this EID function.

3. Δ EIDs due to electronic configuration changes

The Δ EIDs caused by adding an electron to the $2s$, $1s$, $4s$, or $5s$ orbital are shown in figs. 1-2, 1-1s, 1-4s, and 1-5s, respectively. Here, one of the four orbital occupations is increased by one, while the other three occupations and the two nuclear charges are kept constant.

In these figures, the Δ EID is denoted by two circles connected by a solid line or a dashed line, where the upper circle denotes the EID before the addition of an electron and the lower circle denotes the EID after the addition of an electron. The closed circles represent the experimental EIDs, and the open circles the theoretical EIDs. The two circles are connected by a solid line or a dashed line depending on whether both of the two circles are closed or one of them is open. The ordinates of these four plots are molecular charges. The EID data are taken from table 3. The lines in fig. 1 connect data along a diagonal in table 3; for example, data for O_2^{2-} , O_2^{+} , and O_2 with the $4p^2$ configuration (n=0, 1, and 2) configurations give the left and upper most plot in fig. 1-2s.

For each plot in fig. 1, the similarity in the line slopes is apparent. It appears that the slopes are nearly independent of the initial conditions, i.e., the initial EID, the initial molecular charge, and the initial EC. The slopes mainly depend on the nature of the molecular orbital to which an electron is added. This approximate independence of the slopes on the initial conditions has a significant consequence: the Δ EIDs due to any EC change involving the $2s$, $4s$, $5s$, and $1s$ occupations can be predicted by combining the four Δ EIDs that result from a simple $2s$, $4s$, $5s$, or $1s$ ionization (we shall call these Δ EIDs). We further examine this consequence in the following two paragraphs.

Any EC changes can be reduced to a series of extractions and additions of an electron. For example, the EC change resulting from the $5s \rightarrow 2s$ excitation can be reduced to the extraction of an electron from the $5s$ orbital followed by the addition of an electron into the $2s$ orbital. The ΔEID resulting from the extraction of an electron from an orbital is the negative of the ΔEID resulting from the addition of an electron to the same orbital. Furthermore, the ΔEID in each step depends only on the nature of the molecular orbital involved, as mentioned above. Consequently, the ΔEID due to any EC change involving the $2s$, $4s$, $5s$, and $1s$ occupations is just a combination of the four ΔEID s resulting from a simple $2s$, $4s$, $5s$, or $1s$ ionization.

Table 4 compares the predicted and observed ΔEID s due to various excitations and ionizations. The observed ΔEID s are evaluated using experimental EID s in table 3 and averaged for each excitation or ionization. The predicted ΔEID s are calculated with the averaged ΔEID s listed at the top of table 4. A good agreement between the observed and predicted ΔEID s justifies the proposed method. The excitations and ionizations listed in table 4 represent only a fraction of the possible EC changes. The ΔEID s due to other excitations and ionizations can be predicted similarly using the four ΔEID s.

4. ΔEID s due to nuclear charge changes

Fig. 2 shows the ΔEID caused by increasing one of the nuclear charges by one. Here, one of the two nuclear charges is increased, but the other nuclear charge and the EC are kept constant. In the figure, the ordinate is a pair of nuclear charges, and the abscissa is the EID in Å. As in fig. 1, a ΔEID is denoted by two circles connected by a solid line or a dashed line. The closed circles represent the experimental EID s, and the open circles the theoretical EID s. The two circles are connected again by a solid line or a dashed line depending on whether both of the two circles are closed or one of them is open. In fig. 2, the molecular charges of the connected circles always increase successively from the top to the bottom. The molecular charge of the top circle, which is either negative or neutral, is denoted by a minus sign or no sign over the top circle. The EID data are taken from table 3.

In fig. 2, the slopes of the solid lines, the experimental ΔEID s, show a systematic behavior:

- (1) When one of the two nuclear charges is increased by one, the EID always decreases.
- (2) The ΔEID s due to the same nuclear-charge replacement, for example, the C \rightarrow N replacement, resemble each other.
- (3) The decreases in the EID s for the C \rightarrow N, N \rightarrow O, and O \rightarrow F replacements correlate with the decreases in the corresponding atomic radii (Pauling (5)). (See also table 5.)

Table 5 lists the averaged ΔEID for each replacement, which is calculated with experimental EIDs. The averaging for the O-F replacement is done with the O_{2-} and F_{2-} experimental data. As shown in table 5, these averaged $\Delta EIDs$ correlate well with the associated atomic radius (Pauling) changes. In the following section, we investigate the origin of the systematic behaviors mentioned above.

5. Atomic radius overlap

The atomic radius overlap (ARO) of a diatomic molecule is defined in this work as a sum of the two atomic radii minus its EID, where the atomic radii are those given by Pauling (3), namely, 0.77, 0.76, 0.66, and 0.64 Å for C, N, O, and F atoms. The ARO defined as above is an indicator of an averaged atomic orbital overlap in a molecule. When this ARO increases, the orbital energies of antibonding orbitals should increase and those of bonding orbitals should decrease. We first examine the properties of these AROs, then relate them to the systematic behavior observed in the preceding section.

Fig. 3 shows a correlation between the AROs and the $2s \rightarrow 6\sigma$ excitation energies observed in CO, N_2 , NO, and O_2 . The electronic states used to evaluate these $2s \rightarrow 6\sigma$ excitation energies are listed in table 6. In this table, the top four data are obtained from the core-shell electron-energy-loss spectra, and the bottom three data (except the NO- data) from the electron scattering cross sections. For

both experiments, the state energies are measured at the EID of the neutral ground state. Accordingly, the corresponding AROs are calculated as a sum of two atomic radii minus the EID of the neutral ground state. Furthermore, the atomic radius of the atom Z with a core hole is assumed to equal that of the atom $Z+1$. In the figure, the presence of a core hole is indicated by an asterisk. As shown in fig. 3, the AROs correlate surprisingly well with the $2s \rightarrow 6\sigma$ excitation energies. This correlation implies that the ARO is a useful indicator of an averaged atomic orbital overlap.

Using the correlation mentioned above, we can predict the $NO-(6\sigma)-NO-(2s)$ energy difference plotted as a closed circle in fig. 3. The value is reported in table 6. Since the vertical electron affinity of NO is 0.02 eV (3), the shape resonance peak of $NO-(6\sigma)$ should be 15.2 eV. This peak has not been observed yet.

Suppose that in a diatomic molecule or ion, one of the two nuclear charges, Z, is replaced by $Z+1$, keeping the other nuclear charge and the EC constant. This nuclear charge replacement gives a new EID and alters the sum of the two atomic radii, consequently yielding a new ARO. The old ARO (i.e., the $ARO(Z)$ before the nuclear charge replacement), therefore, could differ from the new ARO (i.e., the $ARO(Z+1)$ after the nuclear charge replacement). These $ARO(Z)$ and $ARO(Z+1)$ are plotted in fig. 4. The plotted AROs are calculated with the experimental EIDs in

table 3. Fig. 4 shows that these AROs are nearly identical. (Three deviant points, which are depicted by closed circles, are excluded in the following section.) This means that the value of ARO stays constant against the above-mentioned nuclear charge replacement. This also means that molecules or ions that have an identical EC have an identical ARO, regardless of their nuclear charges under a constraint of $|Z_1 - Z_2| \leq 1$. This property of AROs is here referred to as the ARO conservation law.

The systematic behaviors (1)-(3) described in section 4 originate from the ARO conservation law stated above. According to this conservation law, we have

$$r(Z_1) + r(Z_2) - R(Z_1, Z_2) \approx r(Z_1 + 1) + r(Z_2) - R(Z_1 + 1, Z_2) \quad (1)$$

for molecules or ions that have an identical EC. The $r(Z)$ denotes the atomic radius (Pauling) of atom Z , and the $R(Z_1, Z_2)$ denotes the EID of the molecule or ion with its nuclear charges Z_1 and Z_2 . Rearranging eq. (1), we obtain

$$R(Z_1 + 1, Z_2) - R(Z_1, Z_2) \approx r(Z_1 + 1) - r(Z_1) \quad (2)$$

This eq. (2) is the mathematical expression of the systematic behaviors (1)-(3).

4. Deviations from systematic behavior

In fig. 4, two closed circles at (-0.071, -0.028) and (0.076, 0.105) deviate significantly from the y=x line. These circles arise from the $4p^2 1s^2 5s^2 2s$ and $4p^2 1s^2 5s^2 2s$ ECs, respectively. Also, the EID (1.262 Å) of the $N_2^-(4p^2 1s^2 5s^2 2s)$ produces substantial deviations in figs. 1-2s, 1-1s, and 1-5s. All three ECs mentioned above have the open 1s and 2s shells. Missing terms for these ECs (see table 2) could be responsible for their deviations. For the same reasons, we suspect the averaged EID of the $4p^2 1s^2 5s^2 2s^2$ EC.

The EID (1.268 Å) of the $C_2^-(4p^2 1s^2 5s^2) \approx E_{e^-}$ state causes a substantial deviation in fig. 4, furnishing the third closed circle at (0.298, 0.272). This EID also produces deviant slopes in figs. 1-5s and 1-1s. A smaller EID value for the C_2^- state, 1.24 Å, would bring the deviant circle onto the y=x line. The same EID value also would remedy the deviant slopes in figs. 1-5s and 1-1s. In sum, these three deviations can be corrected coincidentally by a single EID value (1.24 Å). Based on this observation, we propose 1.24 Å for the EID of the $C_2^-(4p^2 1s^2 5s^2) \approx E_{e^-}$ state.

7. EIDs of doubly ionized ions

In table 3, all EIDs of doubly ionized ions are theoretically calculated. In the previous sections, these theoretical EIDs are excluded in the analyses. (In figs. 1 and 2, these theoretical EIDs are denoted with open circles to distinguish the experimental EIDs, which are denoted with

closed circles.) The systematic behaviors found in the previous sections are, therefore, for the $|Q| \leq 1$ systems.

The lower-lying states of some doubly ionized ions often dissociate into two singly ionized atoms. In these cases, the repulsive force due to the two positive charges dominates at a large internuclear distance. This repulsive force for the $Q=2$ system is absent in the $|Q| \leq 1$ systems. Because of this absence, the systematic behaviors observed for the $|Q| \leq 1$ systems must be modified when applied for the $Q=2$ systems.

The EIDs of doubly ionized ions listed in table 3 tend to be longer than those expected from the systematic behaviors found for the $|Q| \leq 1$ systems. (See fig. 2.) Based on this trend, we propose the following procedure to predict the EIDs of doubly ionized ions ($Q=2$). First, use the systematic trends found for the $|Q| \leq 1$ systems to obtain the EIDs. Then, increase these EIDs by

$$\begin{aligned} 0.010 \text{ \AA}, & \text{ if } \text{ARO} \geq 0.2 \text{ \AA} \\ 0.025 \text{ \AA}, & \text{ if } 0.2 \text{ \AA} > \text{ARO} \geq 0.1 \text{ \AA} \\ 0.040 \text{ \AA}, & \text{ if } 0.1 \text{ \AA} > \text{ARO} \geq 0.0 \text{ \AA} \end{aligned} \quad (3)$$

where the ARDs are evaluated with the EID predicted in the first step. If the ARO is less than zero, the repulsive force dominates and thus the procedure is not applicable.

This procedure roughly reproduces the EIDs of doubly ionized ions listed in table 3.

8. Application to CN^-

Assuming the ARO conservation law for the $4\sigma^2 1s^2 5\sigma^2 (\pi^2 \Sigma^-)$ states of CN^- , Na_2 , and ND^- , we have

$$0.77 + 0.70 - r_-(\text{CN}^-) = 0.70 + 0.70 - 1.098(\text{Na}_2) \quad (4)$$

and

$$0.77 + 0.70 - r_-(\text{CN}^-) = 0.70 + 0.66 - 1.063(\text{ND}^-) \quad (5)$$

These two equations yield $r_-(\text{CN}^-) = 1.168$ and 1.173 \AA . The optimal $r_-(\text{CN}^-)$, which satisfies both eqs. (4) and (5) as closely as possible, is the average of the two $r_-(\text{CN}^-)$ values, namely, 1.171 \AA . Assuming the EID linearity for the $4\sigma^2 1s^2 5\sigma^n$ ($n=0, 1$, and 2) states of CN^- , CN , and CN^+ , we have

$$1.173(\text{CN}^+) - 1.172(\text{CN}) = 1.172(\text{CN}) - r_-(\text{CN}^-) \quad (6)$$

This equation yields $r_-=1.171 \text{ \AA}$ for the $\text{CN}-(4\sigma^2 1s^2 5\sigma^2)$ state. This value agrees exactly with the optimal value found from the ARO conservation law. This means that $r_-(\text{CN}^-)=1.171 \text{ \AA}$ is the optimal value that satisfies all three eqs. (4)-(6) as closely as possible. Based on this, we predict $r_-=1.171 \text{ \AA}$ for the CN^- ground state, $4\sigma^2 1s^2 5\sigma^2 (\pi^2 \Sigma^-)$.

The experimental EIDs of CN^- are not yet available.

But, there are several theoretical calculations (9-16) on the EID of the CN^- ground state. Two thirds of them (9-13) are calculated within the SCF level. The most accurate result at this level, the "near Hartree-Fock" limit (13), predicts $r_e = 1.152 \text{ \AA}$ for the CN^- ground state. This EID value deviates significantly from the systematic behaviors. The CI calculations (14-16) are expected to be more accurate than the SCF calculations. Their accuracies in predicting EIDs, however, depend on many factors, such as basis-set size, molecular orbitals used, electronic configurations included, and approximations made to construct and solve the Hamiltonian matrix. The dependence on these factors are interrelated and hard to evaluate. Thus, we cannot judge the accuracy of the predicted EID simply by the computational method used. We must judge its accuracy by the performance in predicting the EIDs for the related systems such as CN , CN^+ , and HCN , whose experimental EIDs are available.

Taylor *et al.* (14) calculated EIDs for HCN , CN , and CN^- using a CI with all double excitations, including some of the higher excitations in the coupled-pair approximation (CPA), and employing the same basis sets for all three systems. The predicted CN bond length (1.151 \AA) in HCN agrees with the experimental bond length (1.153 \AA) (17) to within 0.002 \AA . The predicted EID ($1.170 \pm 0.001 \text{ \AA}$) of the CN ground state also agrees with the experimental EID

(1.172 \AA) (3) to within 0.002 \AA . The EID of the CN^- ground state was predicted to be 1.174 \AA . All three theoretical EIDs cited above were calculated with the same method (CI+CPA) and the same basis. From the results above, the best estimate of the EID for the CN^- ground state is probably $1.174 \pm 0.003 \text{ \AA}$. (Taylor *et al.* estimated it to be $1.173 \pm 0.002 \text{ \AA}$.) This estimate agrees with our empirical estimate (1.171 \AA) indicated at the beginning of this section. These two estimates suggest that the actual EID of the CN^- ground state is around $1.172 \pm 0.003 \text{ \AA}$.

Table 7 compares the predicted EIDs for the CN^- ground state. We believe that our empirical estimate is more accurate than the near Hartree-Fock prediction (13) and some of the results from extensive CI calculations (15,16).

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Table 1

Observed or calculated term energies (cm^{-1}), state symmetries, and electronic configurations for Ca, CN, NO, O₂, FO, F₂, and their ions. The theoretical results are in parentheses.

Number of electrons	Electronic configuration				Symmetry Charges on molecule			
	4g	1s	5p	2s	Q=-1	Q=0	Q=1	Q=2
12	2	4	0	0	1E ⁺	(BC ₂) 0	(CN ⁺) 0	(N ₂ ⁺⁺) (5020)
"	2	3	1	0	3Π	---	---	(0)
"	"	"	"	"	1Π	---	8314	(10290)
"	1	4	1	0	1E ⁺	---	45334	(69480)
"	2	2	2	0	3E ⁻	---	6434	(3370)
13	2	4	1	0	1E ⁺	(C ₂ ⁺) 0	(N ₂ ⁺) 0	(NO ⁺⁺) (0)
"	2	3	2	0	3Π	---	9167	(6700)
"	2	2	2	1	3Π	---	52318	---
"	1	4	2	0	3E ⁻	18391	25461	(38110)
"	2	3	1	1	3E ⁻	---	64608	---
14	2	4	2	0	1E ⁺	(CN ⁺) 0	(NO ⁺) 0	(O ₂ ⁺⁺) (0)
"	2	3	2	1	3E ⁻	---	52190	(47640)
"	"	"	"	"	3E ⁻	---	67220	(71250)
"	"	"	"	"	3E ⁻	---	69340	(74200)
"	"	"	"	"	3Δ	---	61880	---
"	"	"	"	"	1Δ	---	71450	(80620)
"	2	4	1	1	3E ⁺	---	104498	---
"	"	"	"	"	3Π	---	59240	(68330)
"	"	"	"	"	1Π	---	73472	(80660)
15	2	4	2	1	3Π	(N ₂ ⁺) 0	(O ₂ ⁺) 0	(OF ⁺⁺) (0)
"	2	3	2	2	3Π	---	45914	---
"	"	"	"	"	4Π	---	40669	---
"	"	"	"	"	---	---	32964	---
16	2	4	2	2	3E ⁻	(NO ⁺) 0	(OF ⁺) 0	(F ₂ ⁺⁺) (0)
"	"	"	"	"	1Δ	6050	7918	---
"	"	"	"	"	3E ⁻	---	13195	---
17	2	4	2	3	3Π	(O ₂ ⁺) 0	(F ₂ ⁺) 0	(FNe ⁺⁺) (0)
"	"	"	"	"	---	---	---	---
18	2	4	2	4	1E ⁺	(OF ⁺) 0	(FNe ⁺) 0	(Ne ₂ ⁺⁺) (0)

Table 2

Observed or calculated equilibrium internuclear distances (Å), state symmetries, and electronic configurations for Ca^+ , CN^+ , N_2^+ , NO^+ , O_2^+ , F_2^+ , and their ions. The corresponding term energies are given in Table 1. The theoretical results are in parentheses.

Number of electrons	Electronic configuration	Charges on molecule		
		Q_{Ca^+}	Q_{CN^+}	$Q_{\text{N}_2^+}$
12	2 4 0 0 $^1\Sigma^+$	(BC $^-$)	(C $_2$)	(N $_2^{++}$)
"	2 4 0 0 $^3\Sigma^-$	---	1.243	(1.148)
"	2 3 1 0 $^3\Pi$	---	1.312	(1.222)
"	2 3 1 0 $^1\Pi$	---	1.318	(1.235)
"	1 4 1 0 $^1\Sigma^+$	---	1.238	(1.149)
"	2 2 2 0 $^3\Sigma^-$	---	1.369	(1.295)
13	2 4 1 0 $^3\Sigma^+$	(C $_2^{--}$)	(CN)	(N $_2^{--}$)
"	2 3 2 0 $^3\Pi$	---	1.268	(1.172)
"	2 2 2 1 $^3\Pi$	---	1.116	(1.082)
"	1 4 2 0 $^3\Sigma^-$	---	1.233	(1.154)
"	2 3 1 1 $^3\Sigma^-$	---	1.498	1.471
"	2 3 1 1 $^1\Sigma^-$	---	1.223	1.150
"	2 3 1 1 $^3\Sigma^-$	---	1.325	1.262
14	2 4 2 0 $^1\Sigma^+$	(CN $^-$)	(N $_2$)	(O $_2^{++}$)
"	2 3 2 1 $^3\Sigma^-$	---	1.098	(1.010)
"	2 3 2 1 $^3\Pi$	---	1.287	(1.284)
"	2 3 2 1 $^1\Sigma^-$	---	1.278	(1.246)
"	2 3 2 1 $^3\Sigma^-$	---	1.276	(1.239)
"	2 3 2 1 $^3\Pi$	---	1.280	---
"	2 3 2 1 $^1\Sigma^-$	---	1.268	(1.212)
"	2 3 2 1 $^3\Sigma^-$	---	1.444	---
"	2 4 1 1 $^3\Pi$	---	1.213	(1.163)
"	2 4 1 1 $^1\Pi$	---	1.220	(1.175)
15	2 4 2 1 $^3\Pi$	(N $_2^{--}$)	(NO)	(O $_2^{--}$)
"	2 3 2 2 $^3\Pi$	1.19	1.151	1.116
"	2 3 2 2 $^1\Pi$	---	1.416	1.409
"	2 3 2 2 $^3\Sigma^-$	---	---	1.381
16	2 4 2 2 $^3\Sigma^-$	(NO $^-$)	(O $_2$)	(F $_2^{++}$)
"	2 3 2 2 $^1\Sigma^-$	1.25	1.208	---
"	2 3 2 2 $^1\Pi$	1.26	1.216	---
"	2 3 2 2 $^3\Sigma^-$	---	1.227	---
17	2 4 2 3 $^3\Pi$	(O $_2^{--}$)	(OF)	(F $_2^{--}$)
"	2 4 2 3 $^1\Pi$	1.35	(1.32)	1.322
18	2 4 2 4 $^1\Sigma^-$	(OF $^-$)	(F $_2$)	(Ne $_2^{++}$)
"	2 4 2 4 $^3\Sigma^-$	---	1.412	---

Table 3

Equilibrium internuclear distance (Å) averaged for a given electronic configuration. The theoretical results are in parentheses.

Number of electrons	Electronic configuration	Charges on molecule		
		Q_{Ca^+}	Q_{CN^+}	$Q_{\text{N}_2^+}$
12	2 4 0 0	(BC $^-$)	(C $_2$)	(CN $^-$)
"	2 4 0 0	---	1.243	1.173
"	2 3 1 0	---	1.314	1.247
"	1 4 1 0	---	1.238	1.171
"	2 2 2 0	---	1.369	---
13	2 4 1 0	(C $_2^{--}$)	(CN)	(N $_2^{--}$)
"	2 3 2 0	---	1.268	1.172
"	2 2 2 1	---	1.233	1.175
"	1 4 2 0	---	1.498	1.471
"	2 3 1 1	---	1.223	1.150
"	2 3 1 1	---	1.325	1.262
14	2 4 2 0	(CN $^-$)	(N $_2$)	(NO $^+$)
"	2 3 2 1	---	1.098	1.063
"	2 3 2 1	---	1.295	1.284
"	2 3 2 1	---	1.215	1.180
15	2 4 2 1	(N $_2^{--}$)	(NO)	(O $_2^{--}$)
"	2 3 2 2	---	1.19	1.151
"	2 3 2 2	---	1.416	1.390
16	2 4 2 2	(NO $^-$)	(O $_2$)	(OF $^+$)
"	2 3 2 2	1.25	1.214	---
17	2 4 2 3	(O $_2^{--}$)	(OF)	(F $_2^{--}$)
"	2 4 2 3	1.35	(1.32)	1.322
18	2 4 2 4	(OF $^-$)	(F $_2$)	(FNe $^+$)
"	2 4 2 4	---	1.412	---

Table 4

Comparison of observed and predicted EID changes due to excitations and ionizations. Observed changes are obtained from table 3 and averaged. Predicted changes are calculated with the averaged EID changes due to the 2s, 4s, 5s, or 1s ionization, which are listed at the top of this table.

Excitations and ionizations ^a		EID changes (Å)	
		Observed	Predicted
2s → c		-0.103	
4s → c		-0.018	
5s → c		+0.007	
1s → c		+0.111	
<hr/>			
4s → 1s		-0.084	-0.129
4s → 5s		-0.023	-0.025
1s → 5s		+0.098	+0.104
5s → 2s		+0.103	+0.110
1s → 2s		+0.227	+0.214
<hr/>			
2s → c		-0.211	-0.206
4s → c		-0.116	-0.121
5s → c		-0.072	-0.096
1s → c		+0.020	+0.008
1s → 5s		+0.072	+0.118
1s → c		+0.281	+0.222
<hr/>			
2s → 1s		-0.353	-0.317
5s → 1s		-0.205	-0.207
4s → 1s		-0.188	-0.232
4s → 5s		-0.141	-0.128
4s → 1s		-0.062	-0.122
5s → 1s		-0.060	-0.097
1s → 5s		-0.040	+0.001
5s → 4s		+0.022	+0.022
1s → 4s		+0.094	+0.136
1s → 4s		+0.146	+0.240
1s → 5s		+0.164	+0.221
1s → 5s		+0.179	+0.215
1s → 2s		+0.373	+0.325
<hr/>			
4s → 1s		-0.373	-0.243
5s → 1s		-0.341	-0.318
4s → 1s		-0.182	-0.239
4s → 5s		-0.131	-0.233
5s → 1s		-0.126	-0.208

^a c denotes an outgoing electron.

Table 5

Correlation between the AEID due to a nucleus replacement and the associated atomic radius (Pauling) change.

Nucleus replacement	Averaged EID change (Å)	Atomic radius change (Å)
Ca → CN	-0.075	-0.07
CN → N ₂	-0.056	-0.07
C → N (Ave)	-0.066	-0.07
<hr/>		
N ₂ → NO	-0.030	-0.04
NO → O ₂	-0.032	-0.04
N → O (Ave)	-0.031	-0.04
<hr/>		
O → F	-0.014	-0.02

Table 6
Correlation between the $2s-6s$ excitation energies and the atomic radius overlaps. The excitation energies are measured at the EID of the neutral ground state. Accordingly, the atomic radius overlaps are calculated as a sum of the two atomic radii minus the EID of the neutral ground state.

Vertical excitation	Energy (eV)	Overlap (Å)	Reference
$CO(1s\sigma^{-1}6s) - CO(1s\sigma^{-1}2s)$	16.6	0.23	(6)
$N_2(1s\sigma^{-1}6s) - N_2(1s\sigma^{-1}2s)$	17.9	0.26	(6)
$NO(1s\sigma^{-1}6s) - NO(1s\sigma^{-1}2s)$	13.8	0.17	(7)
$O_2(1s\sigma^{-1}6s) - O_2(1s\sigma^{-1}2s)$	9.1	0.09	(6)
$N_2^{-}(6s) - N_2^{-}(2s)$	19.7	0.30	(8)
$NO^{-}(6s) - NO^{-}(2s)$	(15.2) ^a	0.21	---
$O_2^{-}(6s) - O_2^{-}(2s)$	9.8	0.11	(8)

^a Predicted using the trend observed in fig. 3.

Table 7
Comparison of predicted EIDs for the CN^{-} ground state.

References	Method	EID (Å)
Lee and Schaefer [13]	SCF	1.152
Ha and Zumofen [15]	CI	1.198 ^a
Botschwina [16]	CI	1.180 ^a
Taylor <u>et al.</u> [14]	CI	1.173±0.002
This work		1.171

^a with CI⁺ (CI plus higher-order-excitation corrections).

^b with basis B (larger basis set).

Figure Captions

Fig. 1. The ΔEID caused by adding an electron to the $2s$, $1s$, $4s$, or $5s$ orbital. A ΔEID is denoted by two circles connected by a solid or dashed line. The closed circles represent the experimental EIDs, and the open circles the theoretical EIDs. The two circles are connected by a solid or dashed line depending on whether both of the two circles are closed or one of them is open.

Fig. 2. The ΔEID caused by increasing one of the two nuclear charges by one. A ΔEID is denoted by two circles connected by a solid or dashed line. The closed circles represent the experimental EIDs, and the open circles the theoretical EIDs. The two circles are connected by a solid or dashed line depending on whether both of the two circles are closed or one of them is open. The dot-dash lines represent the atomic radius (Pauling) changes due to the nuclear charge increases.

Fig. 3. A correlation between the ARDs and the $2s \rightarrow 6s$ excitation energies observed in CO , N_2 , NO , and O_2 . The data and their references are listed in table 6. The presence of a core hole is indicated by an

asterisk. The solid circle is predicted using the trend observed in this figure.

Fig. 4. The plot of $ARD(Z+1)$ and $ARD(Z)$. The $ARD(Z+1)$ denotes the ARD after one of the two nuclear charges, Z , is replaced by $Z+1$ keeping the other nuclear charge and the EC constant; the $ARD(Z)$ denotes the ARD before this nuclear charge replacement. Each point in the figure represents these paired ARDs. Three deviant points depicted by closed circles are discussed in the text.

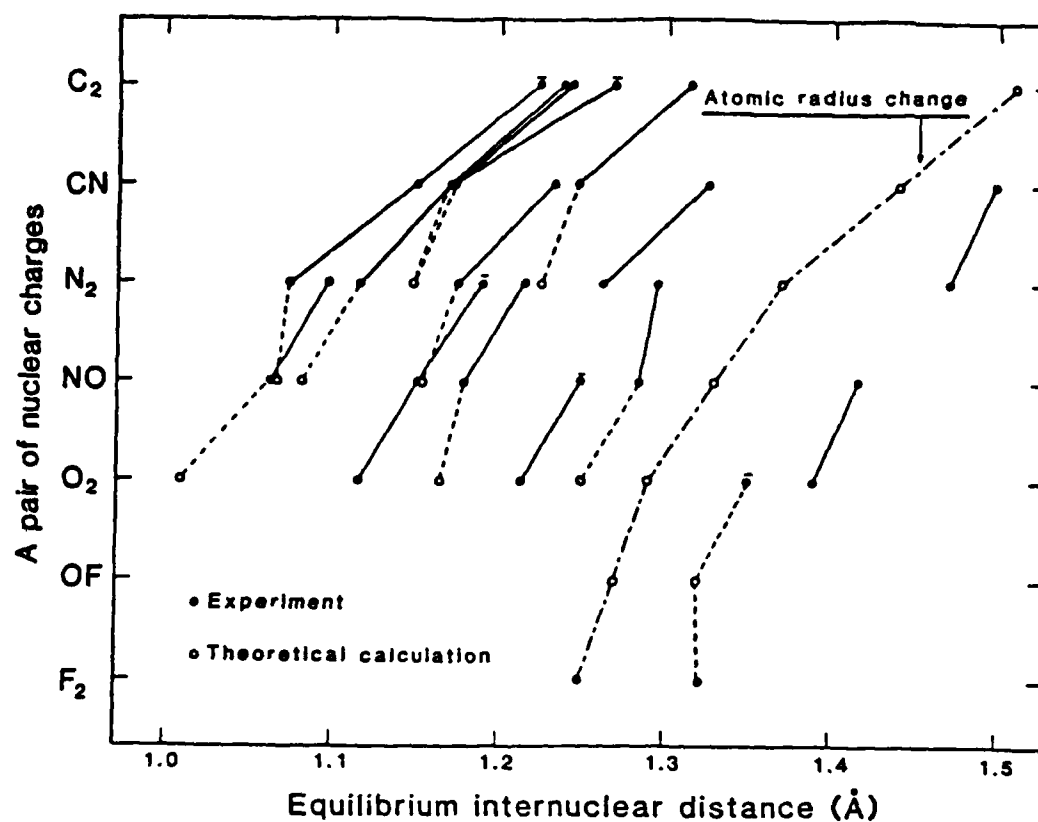


Fig. 2

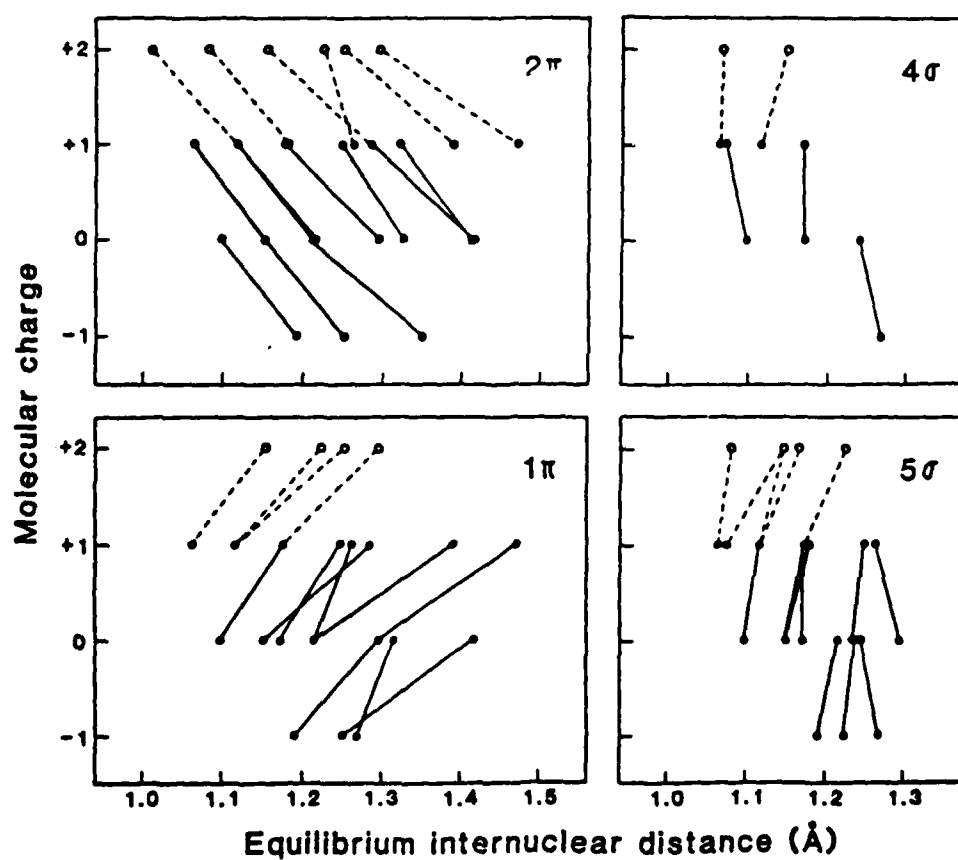


Fig. 1

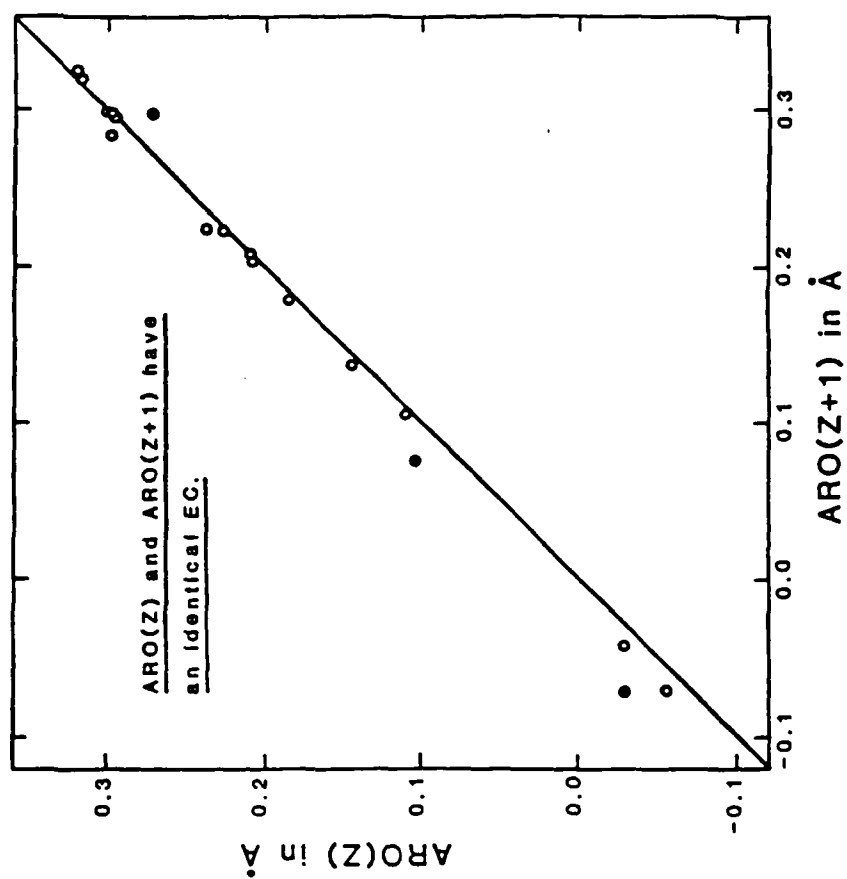
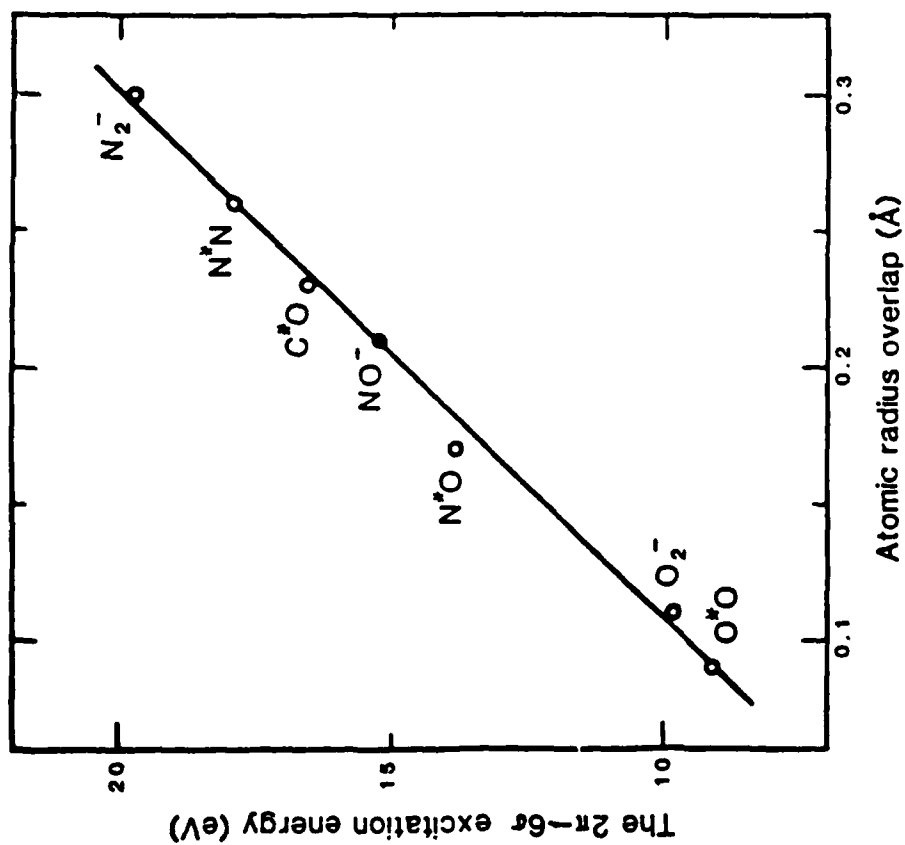


Fig. 3

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